

## Claims

We claim:

1. A multilayer article comprising,  
a metal substrate,  
a first layer comprising an inner and outer surface,  
said first layer comprising a glass/hydroxyapatite admixture comprising a glass composition  
and hydroxyapatite particles (HA),  
said glass composition comprising,  
about 44.2 to about 67.7 wt % SiO<sub>2</sub>, about 10.1 to about 23.4 wt % CaO, about 5.7 to about  
13.3 wt % MgO, about 8.3 to about 23.6 wt % Na<sub>2</sub>O, about 2.2 to about 6.5 wt % K<sub>2</sub>O and  
about 6.0 wt % P<sub>2</sub>O<sub>5</sub>,  
wherein said hydroxyapatite particles are present in the glass/hydroxyapatite admixture in an  
amount of 0.0 wt % to about 50 wt%.

2. The multilayer article of claim 1,  
wherein there is a gradient concentration of the glass/hydroxyapatite admixture which is  
variable over the thickness of the first layer such that there is a higher concentration of  
hydroxyapatite particles nearer the outer surface than the inner surface.

3. The multilayer article of claim 1,  
wherein there is a first intermediate layer having an inner and outer surface,

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~~and said first intermediate layer is located between the substrate and first layer,  
said first intermediate layer comprising a glass composition as defined in claim 1.~~

4. ~~The multilayer article of claim 3,  
wherein the first layer glass/hydroxyapatite admixture has a hydroxyapatite concentration of  
between 10 wt% and 40 wt%.~~

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~~5. The multilayer article of claims 3 or 4,  
wherein there is a second intermediate layer located between the first intermediate layer and  
the substrate,  
said first layer, first intermediate layer and said second intermediate layer all comprising a  
glass/hydroxyapatite admixture as defined in claim 1,  
wherein the hydroxyapatite concentration is highest in the first layer admixture, lowest in the  
second intermediate layer admixture, and present in the first intermediate layer in an amount  
that is in between the first layer and the second intermediate layer.~~

~~6. The multilayer article of claim 5,  
wherein the second intermediate layer has no hydroxyapatite in the admixture,  
the first intermediate layer has 20 wt % hydroxyapatite in the admixture,  
and the first layer has 40 wt % hydroxyapatite in the admixture.~~

7. The multilayer article of claim 6,  
wherein the first layer and the first and second intermediate layers may each independently  
comprise a glass mixture that is a mixture of two or more glasses chosen from the glass  
composition of claim 1.

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8. The multilayer article of claims 1 or 7,  
wherein the substrate is Ti or Ti6Al4V.

9. The multilayer article of claims 3 or 4,  
wherein the glass composition in the first layer comprises about 54.5 wt % SiO<sub>2</sub>, about 15  
wt % CaO, about 8.5 wt % MgO, about 12.0 wt % Na<sub>2</sub>O, about 4.0 wt % K<sub>2</sub>O and about 6.0  
wt % P<sub>2</sub>O<sub>5</sub>,  
and the glass composition in the first intermediate layer comprises  
about 61.1 wt % SiO<sub>2</sub>, about 12.6 wt % CaO, about 7.2 wt % MgO, about 10.3 wt % Na<sub>2</sub>O,  
about 2.8 wt % K<sub>2</sub>O and about 6.0 wt % P<sub>2</sub>O<sub>5</sub>,  
and the substrate is Ti or Ti6Al4V.

10. The multilayer article of claims 3 or 4,  
wherein the glass composition in the first layer comprises about 52.7 wt% SiO<sub>2</sub>, about 12.6  
wt % CaO, about 7.1 wt % MgO, about 17.0 wt % Na<sub>2</sub>O, about 4.6 wt % K<sub>2</sub>O and about 6.0  
wt % P<sub>2</sub>O<sub>5</sub>,  
and the glass composition in the first intermediate layer comprises:

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about 56.5 wt %  $\text{SiO}_2$ , about 15 wt %  $\text{CaO}$ , about 8.5 wt %  $\text{MgO}$ , about 11.0 wt %  $\text{Na}_2\text{O}$ ,  
about 3.0 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$ ,  
and the substrate is Ti or Ti6Al4V.

11. The multilayer article of claims 3 or 4,

wherein the glass composition in the first layer and the first intermediate layer comprise  
about 56.5 wt %  $\text{SiO}_2$ , about 15 wt %  $\text{CaO}$ , about 8.5 wt %  $\text{MgO}$ , about 11.0 wt %  $\text{Na}_2\text{O}$ ,  
about 3.0 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$  and the glass/hydroxyapatite admixture in the  
first layer comprises 50 wt% glass and 50 wt % hydroxyapatite,  
and the substrate is Ti or Ti6Al4V.

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12. The multilayer article of claim 5,

wherein the glass composition in the first layer, the first intermediate layer and the second  
intermediate layer each comprise about 61.1 wt %  $\text{SiO}_2$ , about 12.6 wt %  $\text{CaO}$ , about 7.2 wt  
%  $\text{MgO}$ , about 10.3 wt %  $\text{Na}_2\text{O}$ , about 2.8 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$  and the  
glass/hydroxyapatite admixture in the first layer comprises 60 wt% glass and 40 wt %  
hydroxyapatite,  
and the admixture in the first intermediate layer comprises 80 wt% glass and 20 wt %  
hydroxyapatite and the admixture in the second layer comprises 100 wt% glass and 40 wt %  
hydroxyapatite, and the substrate is Ti or Ti6Al4V.

13. A multilayer article comprising,  
a metal substrate,  
n intermediate layers, where n is an integer,  
a first layer comprising an inner and outer surface,  
said n intermediate layers disposed between the metal substrate and the first layer,  
wherein the n intermediate layers and the first layer each independently comprise a  
glass/hydroxyapatite admixture comprising a glass composition and hydroxyapatite particles  
(HA),  
said glass composition comprising,  
about 44.2 to about 67.7 wt %  $\text{SiO}_2$ , about 10.1 to about 23.4 wt %  $\text{CaO}$ , about 5.7 to about  
13.3 wt %  $\text{MgO}$ , about 8.3 to about 23.6 wt %  $\text{Na}_2\text{O}$ , about 2.2 to about 6.5 wt %  $\text{K}_2\text{O}$  and  
about 6.0 wt %  $\text{P}_2\text{O}_5$ ,  
and wherein said hydroxyapatite particles being present in the glass/hydroxyapatite  
admixture in an amount of 0.0 wt % to about 50 wt%,  
such that the first layer has a hydroxyapatite concentration greater than all layers under it,  
each n intermediate layer under the first layer has a hydroxyapatite concentration greater than  
the n intermediate layer under it,  
so there is a gradient of glass/hydroxyapatite admixtures in the multilayered article such that  
the highest concentration of hydroxyapatite is found in the first layer and the least is found in  
the n intermediate layer next to the substrate.

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wherein the first layer and the  $n$  intermediate layers may each comprise a glass mixture that is a mixture of two or more glasses chosen from the glass composition in claim 20.

wherein the substrate is Ti or Ti6Al4V.

wherein  $n = 1$  and,

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and the glass composition in the n=1 intermediate layer comprises about 61.1 wt % SiO<sub>2</sub>, about 12.6 wt % CaO, about 7.2 wt % MgO, about 10.3 wt % Na<sub>2</sub>O, about 2.8 wt % K<sub>2</sub>O and about 6.0 wt % P<sub>2</sub>O<sub>5</sub>.

wherein  $n = 1$  and

no SiO<sub>2</sub>  
claimed

about 56.5 wt % SiO<sub>2</sub>, about 15 wt % CaO, about 8.5 wt % MgO, about 11.0 wt % Na<sub>2</sub>O,  
about 3.0 wt % K<sub>2</sub>O and about 6.0 wt % P<sub>2</sub>O<sub>5</sub>.

18. The multilayer article of claim 13,

wherein  $n = 1$  and wherein the glass composition in the first layer and the  $n=1$  intermediate layer comprises about 56.5 wt %  $\text{SiO}_2$ , about 15 wt %  $\text{CaO}$ , about 8.5 wt %  $\text{MgO}$ , about 11.0 wt %  $\text{Na}_2\text{O}$ , about 3.0 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$  and the glass/hydroxyapatite admixture in the first layer comprises 50 wt% glass and 50 wt % hydroxyapatite.

19. The multilayer article of claim 13,

wherein  $n=2$ ,

and wherein the glass composition in the first layer and each intermediate layers comprises about 61.1 wt %  $\text{SiO}_2$ , about 12.6 wt %  $\text{CaO}$ , about 7.2 wt %  $\text{MgO}$ , about 10.3 wt %  $\text{Na}_2\text{O}$ , about 2.8 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$  and the glass/hydroxyapatite admixture in the first layer comprises 60 wt% glass and 40 wt % hydroxyapatite, and the admixture in the intermediate layer adjoining the first layer comprises 80 wt% glass and 20 wt % hydroxyapatite and the admixture in the intermediate layer next to the substrate comprises 100 wt% glass and 40 wt % hydroxyapatite.

20. A multilayer article comprising,

a metal substrate,

$n$  intermediate layers, where  $n$  is an integer,

a first layer comprising an inner and outer surface,

said  $n$  intermediate layers disposed between the metal substrate and the first layer,

wherein the n intermediate layers and the first layer each independently comprise a glass/hydroxyapatite admixture comprising a glass composition and hydroxyapatite particles (HA),

said glass composition comprising,

about 44.2 to about 67.7 wt %  $\text{SiO}_2$ , about 10.1 to about 23.4 wt %  $\text{CaO}$ , about 5.7 to about 13.3 wt %  $\text{MgO}$ , about 8.3 to about 23.6 wt %  $\text{Na}_2\text{O}$ , about 2.2 to about 6.5 wt %  $\text{K}_2\text{O}$  and about 6.0 wt %  $\text{P}_2\text{O}_5$ ,

and wherein said hydroxyapatite particles being present in the glass/hydroxyapatite admixture in an amount of 0.0 wt % to about 50 wt%,

such that the first layer has a hydroxyapatite concentration greater than all layers under it,

each n intermediate layer under the first layer has a hydroxyapatite concentration greater than the n intermediate layer under it,

so there is a gradient of glass/hydroxyapatite admixtures in the multilayered article such that the highest concentration of hydroxyapatite is found in the first layer and the least is found in the n intermediate layer next to the substrate,

and the glass composition for each layer is chosen such that there such that the first layer has a  $\text{SiO}_2$  concentration less than all layers under it,

and each n intermediate layer under the first layer has a  $\text{SiO}_2$  concentration less than the n intermediate layer under it,

so there is a gradient of  $\text{SiO}_2$  concentration in the admixtures in the multilayered article such that the highest concentration of  $\text{SiO}_2$  is found in the n intermediate layer next to the substrate and the least is found in the first layer.

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